Moving breathers in bent DNA with realistic parameters

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Recent papers have considered moving breathers (MBs) in DNA models including long range interaction due to the dipole moments of the hydrogen bonds. We have recalculated the value of the charge transfer when hydrogen bonds stretch using quantum chemical methods which takes into account the whole nucleoside pairs. We explore the consequences of this value on the properties of MBs, including the range of frequencies for which they exist and their effective masses. They are able to travel through bending points with fairly large curvatures provided that their kinetic energy is larger than a minimum energy which depends on the curvature. These energies and the corresponding velocities are also calculated in function of the curvature.

Keywords: Intrinsic Localized modes. Discrete breathers. Moving breathers. DNA. Geometry.

1. Introduction

Breathers are localized oscillations in coupled networks of nonlinear oscillators [1]. They have been extensively studied in the last years [2,3,4,5,6]. Under some conditions they can move easily along the network while maintaining their localization [7,8]. A physical system where they may play a significant role is DNA, because the hydrogen bonds between nucleotides are highly nonlinear and their openings can be related to biological processes such as transcription, replication and, in the case of MBs, with the transport of information, energy and charge [9,10].

DNA is also a flexible chain, and the question arises of to what extent MBs are hindered in their movement by the points of bending, or if, on the other hand, these points may have a biological role by trapping breathers and accumulating their energy.

The shape of the DNA molecule is felt because the hydrogen bond is a polar one, and the dipolar interaction between the dipoles is a long-range one which depends on the distances and orientations of the dipoles, and, therefore, on the shape.

Soliton properties in the Discrete Nonlinear Schrödinger Equation framework with dipole-dipole interaction have been considered in Refs. [11,12], among others, whereas MBs in DNA Klein-Gordon models have been studied in Ref. [13] and their interaction with bending points in Ref. [14]. A problem for these studies is the fairly large number of physical parameters that are not well known, among them, crucially, the coefficient of dipole interaction. In this paper we present new quantum chemical calculation that lead to the value of this parameter and investigate its consequences. Moreover, the reduction of the number of parameters allow us to explore the variation of another one, the breather frequency, which previously was considered as fixed.

2. Quantum chemical calculation of the charge transfer

The only quantity that it is needed to implement the dipole–dipole interaction is the *charge transfer* q. It is defined in the following way: if p_0 is the dipole moment of a Watson-Crick hydrogen bond at the equilibrium distance, and it is stretched by a small amount u, the new dipole moment is given to the first order in u by $p = p_0 + q\,u$. The relevant estimations have been obtained in Ref. [13], yielding q values between $-0.0014\,\mathrm{e}$ and $-0.0183\,\mathrm{e}$ for an A-T base pair and between $-0.025\,\mathrm{e}$ and $-0.055\,\mathrm{e}$for a G-C base pair, depending on the quantum-chemical method used. However, these values were obtained only for Watson-Crick base pairs *in vacuo*. In the present work we significantly extend our model, in that we take into account

a) the variation of the dipole moment of the whole nucleoside (base + deoxyribose) pair,

b) the influence of the DNA duplex environment on dipole moments of the nucleoside pairs in question.

We also consider the helical structure of the DNA double strand. The procedure now is as follows: we consider regular homogeneous stacked trimers of nucleoside pairs, namely, adeninosine-thymidine (AT) and guanosine-cytidine (GC) pairs in the following arrangement: AT/AT/AT and GC/GC/GC. We take the 'effective' dipole moment of a nucleoside base pair to be one third of the trimer dipole moment. Then we stretch and squeeze H-bonds by gradually adding or subtracting of up to 0.1 Angstrom to the equilibrium spacing between A and T (or G and C) in the central pair of the trimer, with the two flanking pairs remaining in the standard B-DNA-conformation. At each of the H-bond stretching/squeezing states, the 'effective' dipole moment of a nucleoside pair was estimated using semiempirical quantum chemistry. The relevant computational details are published elsewhere [15].

We evaluate a linear regression of the 'effective' dipole moment (p) onto the nucleotide spacing change (u) in the Watson-Crick pairs ($p = p_0 + q\,u$), where the coefficient q, delivers the desired estimate. As a result, we have obtained $p_0 = 1.84\,\mathrm{D}$, $q = -0.09\,\mathrm{e}$, for the AT pair and $p_0 = 3.15\,\mathrm{D}$, $q = -0.10\,\mathrm{e}$, for the GC pair. The Watson-Crick H-bond stretching diminishes the effective dipole moment of nucleoside pairs, which ought to be connected with the proper changes in the purine-pyrimidine molecular orbital overlap included into quantum-chemical evaluations of dipole moments. If we take into account only the conventional electrostatic charge distributions, increasing the spacing between the partners in the Watson-Crick base pair should lead to the increase in the dipole moment. Note that the values of q obtained in this way are substantially larger than the ones obtained in Ref. [13] and very similar for both the A-T and G-C pairs, in spite of the different number of hydrogen bonds. This could be explained by the appreciable influence of the DNA duplex surrounding on the Watson-Crick A-T and G-C base pair dipole moments. We agree that taking an "effective" dipole moment of the stacked base pair trimer is only an approximation. We intended to include the coupling between the nearest neighbours in the DNA stack. That the "effective" dipole moment values differ from those of the isolated base pairs is actually a significant result showing that we were right to include the DNA stacking interactions at least approximately into our model. As to the Coulomb electron-electron interaction, it was considered at our Hartree-Fock-level quantum-chemical calculations in the form of Pauli correlations, where electrons of the same spin are repellent. Note also that being the values of q for both homopolynucleotide duplexes very similar we should not expect q to change significatively for heterogeneous DNA.

3. The model

The Hamiltonian system also used in Ref. [13,14] is a Peyrard–Bishop model [16] augmented with long-range interaction. It can be written as:

$$H = \sum_{n=1}^{N} \Big(\frac{1}{2} m \dot{u}_n^2 + D\,(e^{-b\,u_n} - 1)^2 + \\ \frac{1}{2} k\,(u_{n+1} - u_n)^2 + \frac{1}{2} \sum_i J_{in} u_i\, u_n \Big). \tag{1}$$

The explanation of the terms and variables is as follows: u_n is the stretching of the n-th hydrogen bond; m is the reduced mass of a nucleotide pair; the Morse potential $D\,(e^{-b\,u_n} - 1)^2$, represents the energy of a hydrogen bond between a pair of nucleotides; $\frac{1}{2}k\,(u_{n+1} - u_n)^2$ is the stacking energy between neighboring bonds; $\frac{1}{2}\sum_i J_{in} u_i\, u_n$ is the energy of the dipole–dipole interaction; if $\vec{r}_n$ is a vector that denotes the position of each particle in the 2-d space, $J_{in} = J/|\vec{r}_n - \vec{r}_i|^3$, for $i \neq n$ and 0 otherwise, where J, hereafter referred to as the dipole parameter, is given by $J = q^2/(4\,\pi\epsilon_0\,d^3)$, q and $d = 3.4$ Å, being the charge transfer and the distance between neighbouring base pairs, respectively, as deduced in Ref. [13]. We

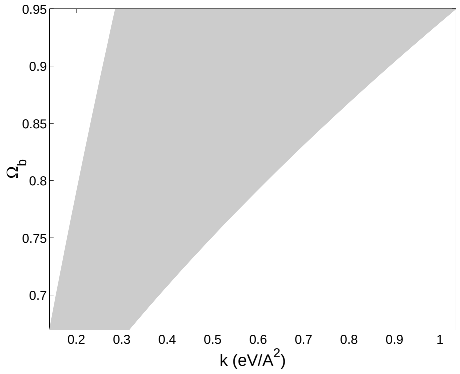

Fig. 1. Range of existence of moving breathers. The upper limit corresponds to the bifurcation of stability inversion. The lower limit is the top frequency of the phonon band. The dispersion is smaller if closer to the upper limit.

approximate the shape of the molecule in the vicinity of a bending point by a parabola with curvature κ embedded in a plane, and consider the dipoles with the same orientation and orthogonal to it. We consider fixed geometry as the H–bond vibrations are much faster than the bending movement. Thus, $\vec{r}_n = (x_n, y_n)$ with $y_n = \kappa x_n^2/2$. We also neglect the heterogeneity of DNA.

The values of the parameters are taken from Ref. [13], i.e., $D = 0.04$ eV, $b = 4.45$ Å^{-1} and $m = 300$ amu. As discussed in the same reference, k can take values between 0.01 eV/Å^2 and 10 eV/Å^2 and, in consequence, we consider it as an adjustable parameter in that range. The value of J for a charge transfer q intermediate between the A-T and G-C base pairs is $J = 0.0031$ eV/Å^2.

4. Moving breathers in a straight chain

Breathers, exact to machine precision, are calculated numerically using techniques based in the anti-continuous limit [17]. MBs with good movability properties, i.e., low dispersion, are obtained for values of the parameters in the vicinity of a bifurcation point, called *inversion of stability*, where a single breather becomes unstable and a double one stable, or vice versa, and perturbing them with a vector collinear to the eigenvector that becomes unstable [7,8].

The particles of the breather oscillate coherently with a frequency ν_b. For the sake of simplicity, we define the non-dimensional frequency $\Omega_\mathrm{b} = \nu_\mathrm{b}/\nu_\mathrm{o}$, where ν_o, defined through

$$\nu_\mathrm{o} = \frac{1}{2\pi}\sqrt{\frac{2b^2 D}{m}} = 1.13 \text{ THz} \qquad (2)$$

is the linear frequency of the isolated oscillators in Eq. 1. As the on–site potential is soft, $\Omega_\mathrm{b} < 1$. We have limited its values to the interval $(0.65, 0.95)$ because lower

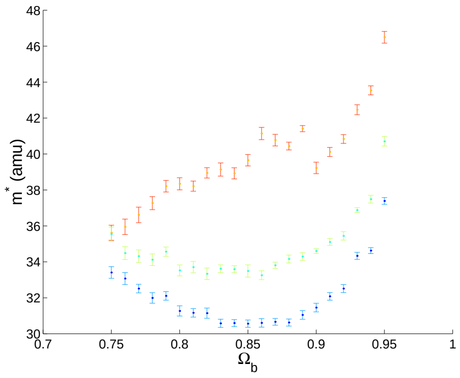

Fig. 2. Dependence of the effective mass m^* with respect to the breather frequency for three different values of the coupling constant k: 0.2376, 0.2693 and 0.3010 eV/Å^2 from bottom to top.

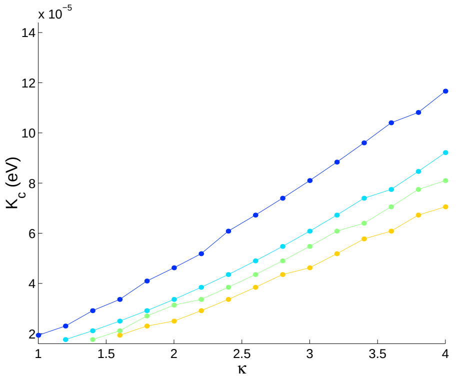

Fig. 3. Dependence of the critical translational energy K_c with respect to κ for $k = k_{\mathrm{s}}$. The frequencies Ω_{b} of the breathers are (from up to down) 0.95, 0.90, 0.85, and 0.80. Smaller values of κ are not shown as K_c is very small and no accurate results can be obtained.

frequencies brings about breathers difficult to move, due to their small width, and MB with larger ones develop frequencies which interact with the phonon band. The latter is due to the fact that MBs are a wave packet with frequencies around the one of the perturbed static breather.

For a given value of the breather frequency Ω_{b}, MBs exist for values of k above a critical one $k_{\mathrm{s}} = k_{\mathrm{s}}(\nu_{\mathrm{b}})$, for which the inversion of stability takes place. This value has to be calculated numerically.

The phonon band is composed of the frequencies of the linear modes, given

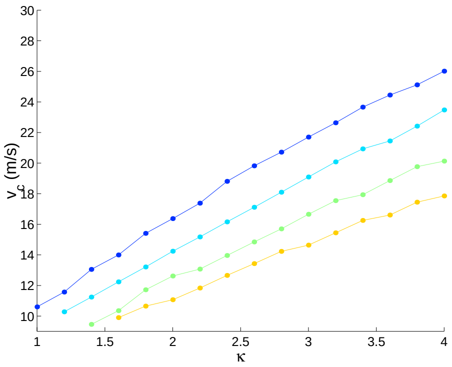

Fig. 4. Same as Fig. 3 but for the critical initial translational velocity (v_c).

by [13,12]:

$$\Omega_{ph}^2 = \left(\frac{\omega_{ph}}{\omega_{\rm o}}\right)^2 = 1 + \frac{4k}{m\,\omega_{\rm o}^2}\,\sin^2\frac{q}{2} + \frac{2J}{m\,\omega_{\rm o}^2}F_3(\Re(e^{iq})), \tag{3}$$

where q is the wave number, $\omega_{\rm o} = 2\,\pi\,\nu_{\rm o}$ and $F_s(z) = \sum_{k>1} z^k/k^2$ is the Polylogarithmic or Jonquière function. They exist for increasing values of $k > k_{\rm s}$ until an upper limit $k_m = k_m(\nu_{\rm b})$, for which the top of the phonon band, at $q = \pi$, reaches the second harmonic of the breather. k_m is given by

$$k_m = \left(\Omega_{\rm b}^2 - \frac{1}{4}\right)\,m\,\omega_{\rm o}^2 + \frac{3}{8}\,J\,\zeta(3)\,, \tag{4}$$

where $\zeta(s)$ is the Riemann's zeta-function. This is also the upper limit for MBs existence. Fig. 1 shows the range of existence of MBs. It can be seen that they exist for a wide range of frequencies, but they have much smaller dispersion at the vicinity of the inversion stability curve and we will restrict often our study to them.

Static breathers in the above mentioned region have an energy between $\mathrm{K_B T}$ and 3.7 $\mathrm{K_B T}$, with $T = 310$ K. The dipolar energy of these breathers oscillates between 0.006 $\mathrm{K_B T}$ and 0.023 $\mathrm{K_B T}$. The energy depends monotonically with the frequency, corresponding the highest energy to the smallest frequency.

Moving breathers behave as quasiparticles, having an effective mass m^* related with the kinetic energy of the breather by $K = \frac{1}{2}m^*\,v^2$, with v being the translational velocity of the breather [7,8]. $K \in (1.5, 50) \times 10^{-4}$ $\mathrm{K_B T}$ is also the kinetic energy added to the static breather. m^* is approximately constant as long as v is small enough and, therefore, emits small phonon radiation. Fig. 2 shows the dependence of the mass with respect to the frequency for three different values of k.

Thus, MBs have an effective mass m^* between 30 and 46 amu, depending on the value of frecuency and the stacking parameter.

5. Moving breathers in bent chains

In order to study the effect of the curvature on breather mobility, we launch a breather through the bending point. The bending acts as a potential barrier [14] in accordance to the trapping hypothesis formulated in Ref. [18] (for a discussion of this last point see Ref. [19]). It implies that breathers are reflected when reaching the bending point as long as their translational energy K is below a critical point K_c. Fig. 3 shows the dependence of this value with respect to κ for several frequencies. The dependence of the critical initial velocity is also shown in Fig. 4. K_c, which is also the amount of energy given to a static breather to start its movement, is fairly small compared to the thermal energy at physiological temperature of 0.027 eV. Therefore, it seems likely that it can be given easily by the environment, and most MBs are able to pass through bending points without being reflected.

6. Conclusion

In this paper we consider a model for DNA with long–range interaction due to the dipole moments of the hydrogen bonds among nucleotides. The dipole parameter J has been obtained through quantum chemical calculations including the whole nucleoside. The consequences for moving breathers in straight and bent DNA chains have been analyzed. These can be summarize as: 1) For each different value of the stacking parameter there exist MBs with different frequencies, including an upper limit, determined numerically for the inversion of stability curve, and a lower limit determined both numerically and analytically by the top of the phonon band. 2) MBs breather have a fairly large effective mass of 30–50 amu. 2) The values of J, though small, are large enough for the MBs to feel the the bending of DNA. 3) We have calculated the minimum kinetic energy and the velocity of a breather to be able to pass over a bending point in function of the curvature. As the minimum kinetic energy is small, it seems plausible that most MBs will have enough energy to pass through bending points, although the ones with low energy will be reflected.

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References

1. R S MacKay and S Aubry. Proof of existence of breathers for time-reversible or Hamiltonian networks of weakly coupled oscillators. *Nonlinearity*, 7:1623, 1994.
2. S Aubry. Breathers in nonlinear lattices: Existence, linear stability and quantization. *Physica D*, 103:201, 1997.
3. S Flach and C R Willis. Discrete breathers. *Phys. Rep.*, 295:181, 1998.
4. Localization in nonlinear lattices. *Physica D*, 119:1–238, 1999. Focus issue edited by S. Flach and R. S. Mackay.

5. R S MacKay. Discrete breathers: classical and quantum. *Physica A*, 288:175, 2000.
6. Nonlinear localized modes: physics and applications. *Chaos*, 13:586–799, 2003. Focus issue edited by Yu. S. Kivshar and S. Flach.
7. Ding Chen, S Aubry, and G P Tsironis. Breather mobility in discrete ϕ^4 lattices. *Phys. Rev. Lett.*, 77:4776, 1996.
8. S Aubry and T Cretegny. Mobility and reactivity of discrete breathers. *Physica D*, 119:34, 1998.
9. M Peyrard and J Farago. Nonlinear localization in thermalized lattices: application to DNA. *Physica A*, 288:199, 2000.
10. M Peyrard. Nonlinear dynamics and statistical physics of DNA. *Nonlinearity*, 17:R1–R40, 2004.
11. P L Christiansen and et al. Solitary excitations in discrete two-dimensional nonlinear schrödinger models with dispersive dipole-dipole interactions. *Phys. Rev. B*, 57:11308, 1998.
12. Yu B Gaididei, S F Mingaleev, P L Christiansen, and K Ø Rasmussen. Effects of nonlocal dispersive interactions on self-trapping excitations. *Phys. Rev. E*, 55:6141–6150, 1997.
13. J Cuevas, J F R Archilla, Yu B Gaididei, and F R Romero. Moving breathers in a DNA model with competing short- and long-range dispersive interactions. *Physica D*, 163:106, 2002.
14. J Cuevas, F Palmero, J F R Archilla, and F R Romero. Moving breathers in a bent DNA model. *Phys. Lett. A*, 299:221, 2002.
15. D Hennig, E Starikov, J F R Archilla, and F Palmero. Charge transport in poly(dG–poly(dC) and poly(dA)-poly(dT) DNA polymers. *Jou. Bio. Phys.*, 2003. To appear, `arXiv:nlin.PS/0308003`.
16. M Peyrard and A R Bishop. Statistical mechanics of a nonlinear model for DNA denaturation. *Phys. Rev. Lett.*, 62:2755, 1989.
17. J L Marín and S Aubry. Breathers in nonlinear lattices: Numerical calculation from the anticontinuous limit. *Nonlinearity*, 9:1501, 1996.
18. J Cuevas, F Palmero, J F R Archilla, and F R Romero. Moving discrete breathers in a Klein–Gordon chain with an impurity. *J. Phys. A: Math. and Gen.*, 35:10519, 2002.
19. J F R Archilla, Yu B Gaididei, P L Christiansen, and J Cuevas. Stationary and moving breathers in a simplified model of curved alpha–helix proteins. *J. Phys. A: Math. and Gen.*, 35:8885, 2002.